Report:

Weathering study on LDPE (with and without d_2w/oxo-biodegradable additive)

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1. Introduction

The purpose of this study is to investigate the effect, if any, of recyclate from oxo-biodegradable plastic shopping bags if such recyclate were used in the manufacture of thick cross-section plastic products intended for long term use outdoors. Such products include plastic lumber, garden and municipal furniture, and signage posts.

However, recyclate from shopping bags would not normally be used for this purpose, and would more likely be used to make short-life items such as shopping bags, trash bags, and bin liners.

Nevertheless, we have been asked by Symphony to advise what would happen in the unlikely event that recyclate from oxo-biodegradable shopping bags were used in the manufacture of thick cross-section plastic products.

In addition, as oxo-degradation is dependent upon oxygen, the thickness of the material limits the penetration of oxygen into the body of the plastic. Therefore, the thicker the material, the less susceptible to oxo-degradation it will be [1].

An important point to remember is that thick cross-section plastic products intended for use outdoors should always contain a UV stabiliser whether or not they contain any oxo-biodegradable recyclate. The stabiliser is there to protect the products from the damaging effects of sunlight, and more general weathering influences, and they would not otherwise be fit for purpose.

The aim of this study was to investigate the effects of sunlight and weathering on recycled LDPE products containing oxo-biodegradable recyclate as compared with recycled LDPE products without such recyclate. We therefore exposed LDPE specimens of the same thickness and for the same length of time, as follows:

(a) conventional reprocessed LDPE as a control, without any oxo-biodegradable recyclate or UV stabiliser and

(b) the same material containing UV-stabiliser but no oxo-biodegradable recyclate, and

(c) the same material containing oxo-biodegradable recyclate but no UV-stabiliser, and

(d) the same material containing UV-stabiliser and oxo-biodegradable recyclate.

2. Materials and Methods

The LDPE grade used in this study was FA6224 from Borealis with a melt flow rate of 2.1 g/10 min at 190°C and 2.16 kg. LDPE was chosen here as it is the most unstable of the commonly used polymers in regard to photo-oxidative degradation [2], and is therefore the worst-case scenario.

We have again chosen the worst case scenario by using samples made from entirely recycled polymer material, which is a very unlikely scenario in practice. In reality it is likely that recyclate would be mixed with virgin polymer, and oxo-biodegradable material is likely to contribute part only of the overall recycled material.

We used as the oxo-biodegradable additive, d_2w (grade 93390), which is based on a polyethylene carrier resin.

Two base films (180 µm thick) were produced at a Reifenhäuser blown film line with a screw diameter of 70 mm, equipped with a barrier screw. One was the unmodified LDPE (referred to here as LDPE-film), the other the LDPE containing 1 % of d_2w 93390 (referred to here as oxo-film). In each case 800 kg of blown film was produced at 175 – 180 °C set barrel temperatures and a throughput of approximately 70 kg/h.

These films were then used in the mechanical recycling step, where an Erema 1108TE recycling machine with a hot die pelletizer was used to regrind the films to pellets again at about 200 °C barrel temperature and a throughput of 420 – 450 kg/h. These pellets are referred to as LDPE pellets and oxo-LDPE pellets.

These pellets were then injection-moulded (Engel Victory 150) to yield 4 mm thick test-plaques.

The UV stabiliser used was a masterbatch containing 10 wt% of Chimassorb 944 in LDPE, produced via twin-screw compounding. This was added at a ratio of 10 wt% to both LDPE and oxo-LDPE, to yield stabilised plaques. This stabiliser is commercially available and is widely used.

Table 1: Recycled film formulations investigated in this study

Formulation	Oxo-LDPE Pellet from recycled oxo film-ex Erema (%)	LDPE Pellet from recycled control film-ex Erema (%)	Masterbatch of 10% Chimassorb 944 in LDPE (%)
(a)	0	100	0
(b)	0	90	10
(c)	100	0	0
(d)	90	0	10

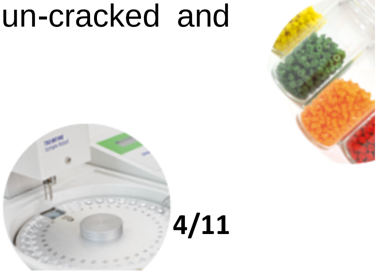
The samples were aged in a Weather-O-Meter according to ISO 4982-2, cycle 1 (102 min UV radiation, 60 w/m², and 18 min of deionized water spray in the absence of UV, for 1000 h. These conditions are much more severe than would be experienced in sunlight, even in locations such as Florida.

From the samples, small cylinders were punched out, and sliced by means of a sharp blade to yield outer layer and bulk samples after the 1000 h cycle. These were investigated by FTIR in ATR-mode (attenuated total reflection) to yield the increase in carbonyl index at 1714/2920 cm^{-1} and afterwards the sample surface was inspected with an optical microscope to observe any changes in the general structure.

3. Results and Discussion

After the weathering cycle of 1000 h, the samples were taken from the device and were visually inspected. The first inspection revealed some surface defects in the samples without UV stabilisation, and these were then inspected by means of a microscope. The micrographs are shown in Figure 1, where one can clearly see the surface cracks in the unstabilised materials, regardless of whether oxo-biodegradable recyclate was present or not.

The presence of oxo-biodegradable recyclate seems to influence the materials a little, because the number of cracks is higher than for the LDPE without oxo-biodegradable recyclate. However, the UV-stabiliser was found to prevent this effect, whether oxo-biodegradable recyclate is present or not, because the UV stabiliser inhibits the propagation of free-radicals which are responsible for polymer degradation. Both stabilised samples therefore exhibit a smooth, un-cracked and uninfluenced surface.



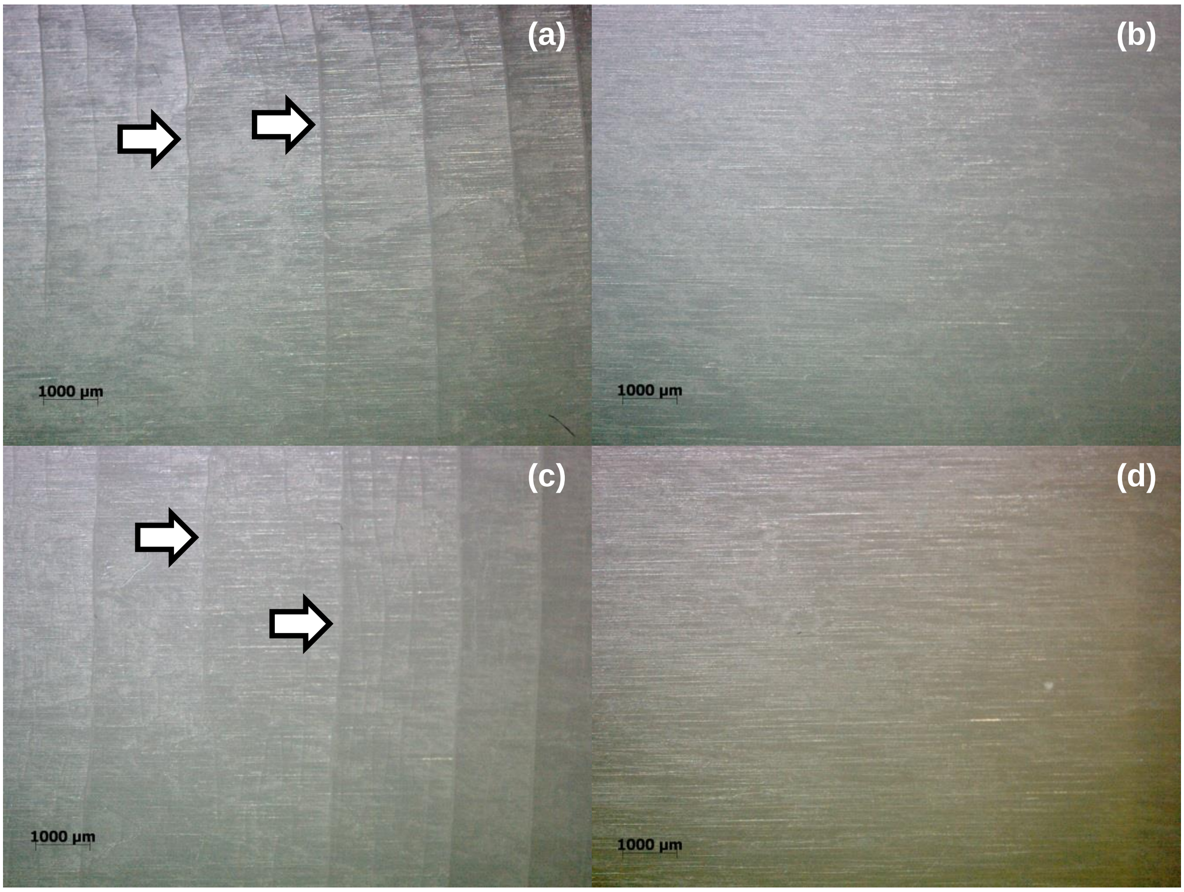


Figure 1: Optical micrographs of the weathered surfaces of the different LDPE; (a) recycled LDPE, (b) recycled LDPE with UV-stabiliser, (c) recycled oxo-LDPE, (d) recycled oxo-LDPE with UV-stabiliser. Arrows indicate examples of surface cracks.

Measuring the ATR-FTIR spectra of the different samples shows the degradation products of the oxidative degradation mechanism in LDPE due to weathering via the carbonyl bands, e.g. found at 1714 cm^{-1} (ISO 10640 “Plastics - Methodology for assessing polymer photo-ageing by FTIR and UV visible spectroscopy”). As can be seen from the following spectra, in all of them only the weathered surface (marked “outside 1000 h”) is exhibiting pronounced peaks in this region. These are more visible for the un-stabilised materials (LDPE and oxo-LDPE, Figure 2 and Figure 4) and less visible for the materials containing UV-stabiliser (Figure 3 and Figure 5). The peaks visible in the latter at approx. 1650 and 1750 cm^{-1} are due to the UV-stabiliser added to these samples.

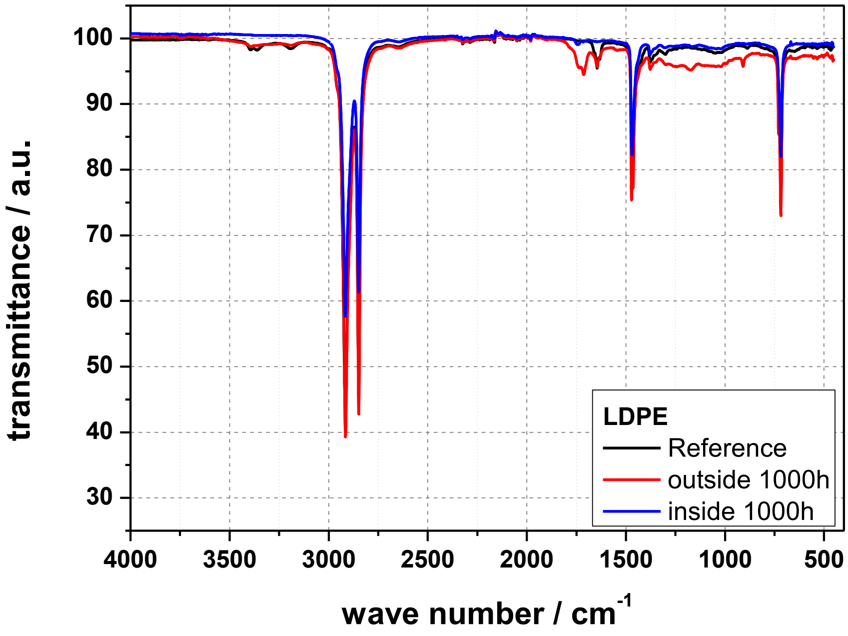


Figure 2: ATR-FTIR spectra of the LDPE before (reference) and after 1000 h of accelerated weathering; “outside” refers to the directly weathered side, and “inside” is 2 mm below the surface of the 4 mm plaque

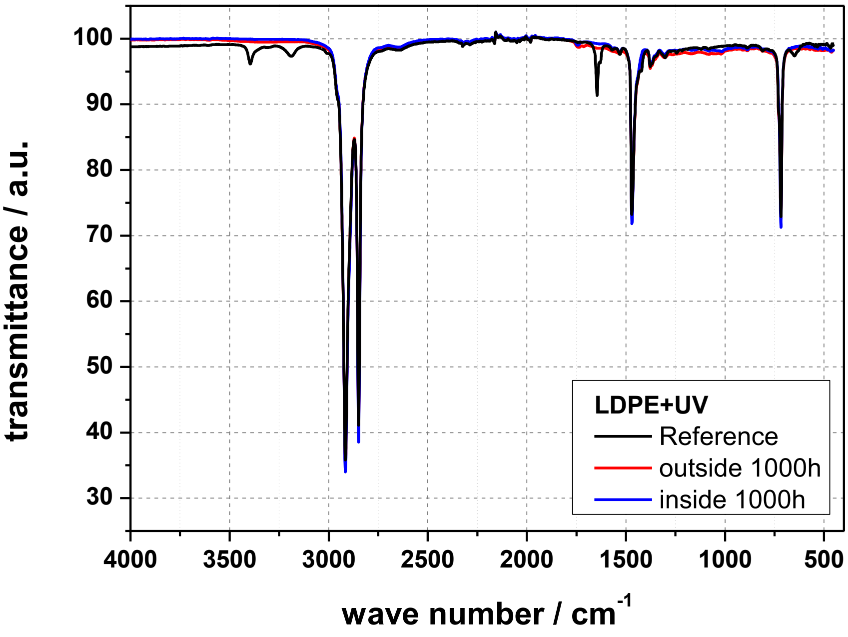


Figure 3: ATR-FTIR spectra of the LDPE with UV-stabiliser before (reference) and after 1000 h of accelerated weathering. “outside” refers to the directly weathered side, and “inside” is 2 mm below the surface of the 4 mm plaque

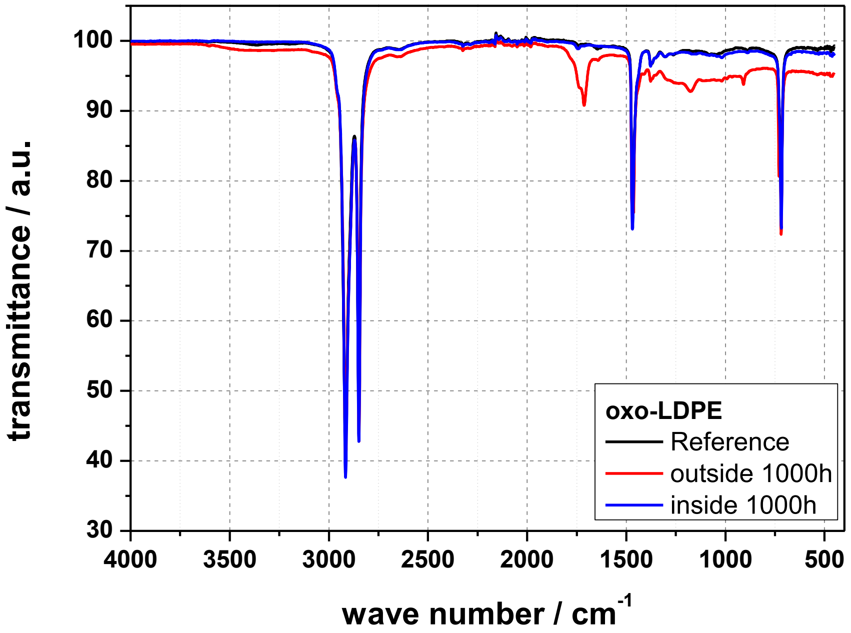


Figure 4: ATR-FTIR spectra of the oxo-LDPE before (reference) and after 1000 h of accelerated weathering. “outside” refers to the directly weathered side, and “inside” is 2 mm below the surface of the 4 mm plaque

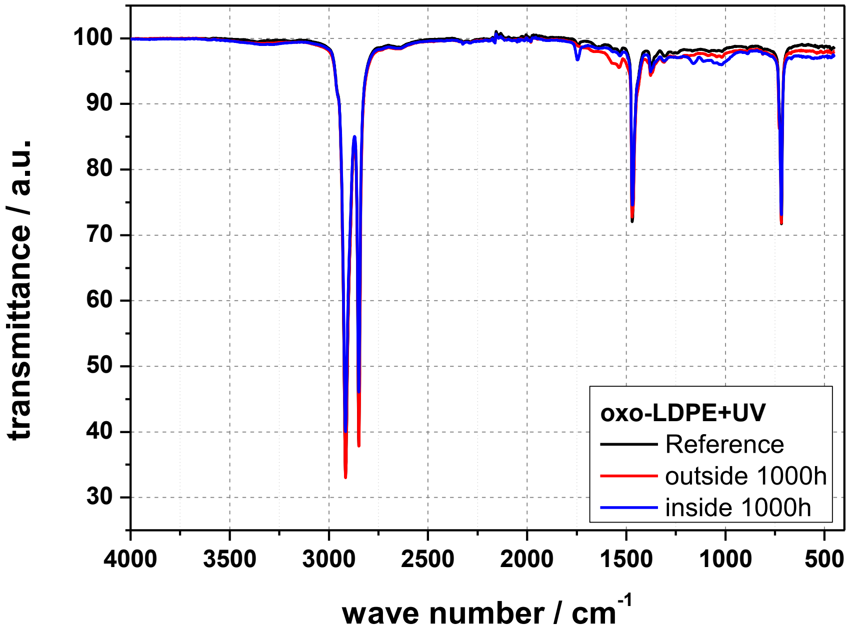


Figure 5: ATR-FTIR spectra of the oxo-LDPE with UV-stabiliser before (reference) and after 1000 h of accelerated weathering. “outside” refers to the directly weathered side, and “inside” is 2 mm below the surface of the 4 mm plaque.

As a more detailed evaluation the carbonyl index is used as a comparison, where the absorbance at 1714 cm-1 is referred to the one at 2920 cm-1 and the carbonyl index value of the according reference sample is subtracted. What we can see from this evaluation (Figure 6), is that the unstabilised materials (conventional and oxo) exhibit an increase in carbonyl index. The oxo-LDPE exhibits a slightly higher value.

We see that adding UV-stabiliser greatly reduces the carbonyl index for the weathered outside surface. For the inside, i.e. the samples taken 2 mm below the surface of the 4 mm plaque, we see some reduction in carbonyl index for the oxo-LDPE and some increase for the LDPE. However, that can be due to the fact that a carbonyl index as low as this is not reliable. Small deviations in the measured data will have a great effect here, and therefore these data points have not been evaluated further.

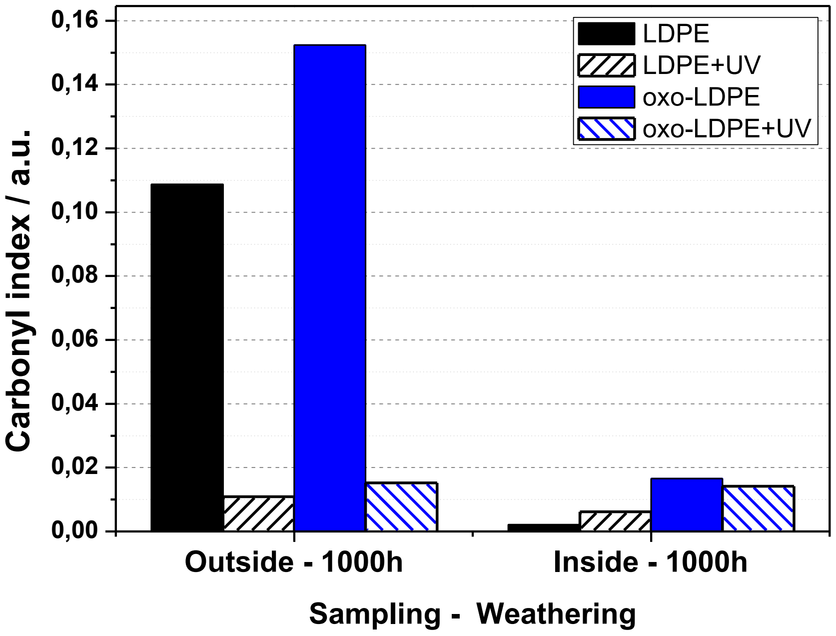


Figure 6: Carbonyl indices calculated from the spectral data of LDPE and oxo-LDPE, with and without UV-stabiliser after 1000 h of accelerated weathering. “outside” refers to the directly weathered side, and “inside” is 2 mm below the surface of the 4 mm plaque.

4. Conclusion

We have observed degradation and evidence of failure in the unstabilised conventional and oxo-biodegradable recycled samples during weathering. There appears to be an effect of the oxo-biodegradable recyclate on the behaviour of unstabilised materials, as evidenced by increased surface cracking, but this is also visible in the reprocessed LDPE containing no oxo-biodegradable additive, though somewhat less pronounced.

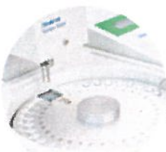
FTIR spectroscopy confirms significantly increased oxidation at the surface only, of both unstabilised test samples after weathering. Evaluation of the FTIR-spectra confirms however that inside the sample, where oxygen is not available, no significant oxidation has been found in any of the samples.

The surface degradation in the unstabilised samples, both with and without the oxo-biodegradable recyclate, will contribute to aesthetic and mechanical failure following exposure to sunlight in the environment. This demonstrates the necessity for UV stabilisation of plastic products made from conventional or oxo-biodegradable recyclate and intended for outdoor use.

UV-stabiliser in both materials greatly improves the surface appearance and mechanical properties after weathering, as can be seen from the micrographs presented here. In addition, the surface also shows less surface degradation in the FTIR spectra of both stabilised samples, thus showing the effectiveness of a UV-stabiliser, whether oxo-degradable recyclate is present or not. All these findings are supported by the carbonyl index evaluation which demonstrates a significant reduction in total polymer oxidation compared to the equivalent unstabilised samples.

This means, that provided a UV-stabiliser has been included (which as demonstrated should always be the case with plastic products intended for outdoor use) there will be no negative effects from the inclusion of oxo-biodegradable recyclate.

These studies also demonstrate that even without UV stabiliser the presence of oxo-biodegradable recyclates has no effect within the body of the plastic, where oxygen is not available.



5. References

1. Cunliffe A.V. and Davis A. Photo-oxidation of thick polymer samples – Part II: The influence of oxygen diffusion on the natural and artificial weathering of polyolefins, 4 Polymer Degradation and Stability (1982) 17-37

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6. Appendix

DI Dr. **Christoph Burgstaller** holds a diploma as well as a PhD in chemical engineering from Johannes Kepler University in Linz and has more than 10 years of experience in plastics industries. Currently he holds the position of managing director and head of R&D at TCKT. He worked in many different projects on materials development, including blends and composites, fillers and reinforcements as well as polymer stabilisation and processing. One part of his work is dedicated to the recycling of thermoplastic materials, with emphasis on reactive processing and compatibilisation of inseparable plastic waste streams. He is a lecturer at the University of Applied Sciences in Wels for materials science, i.e. for composites and lightweight polymeric materials, as well as for organic chemistry. He supervised more than 20 master and bachelor students for the preparation of their thesises. He is a senior member of the Society of Plastics Engineers and has published his work in over 50 national and international conferences, as well as in several peer-reviewed papers.

DI **Volker Reisecker** holds a diploma in plastics engineering from the Mountains University of Leoben and is the deputy director and head of industry orders at TCKT. He has more than 10 years of experience in heading the test laboratory at TCKT, dealing with different aspects of plastics materials investigations, e.g. solid plastics, films, fibres and composites. Furthermore, he is experienced with different aspects of polymer processing and the incorporation of nano-materials in plastics. He is a lecturer at University of Applied Sciences in Wels for materials testing and characterisation and has supervised several master and bachelor students while their work.